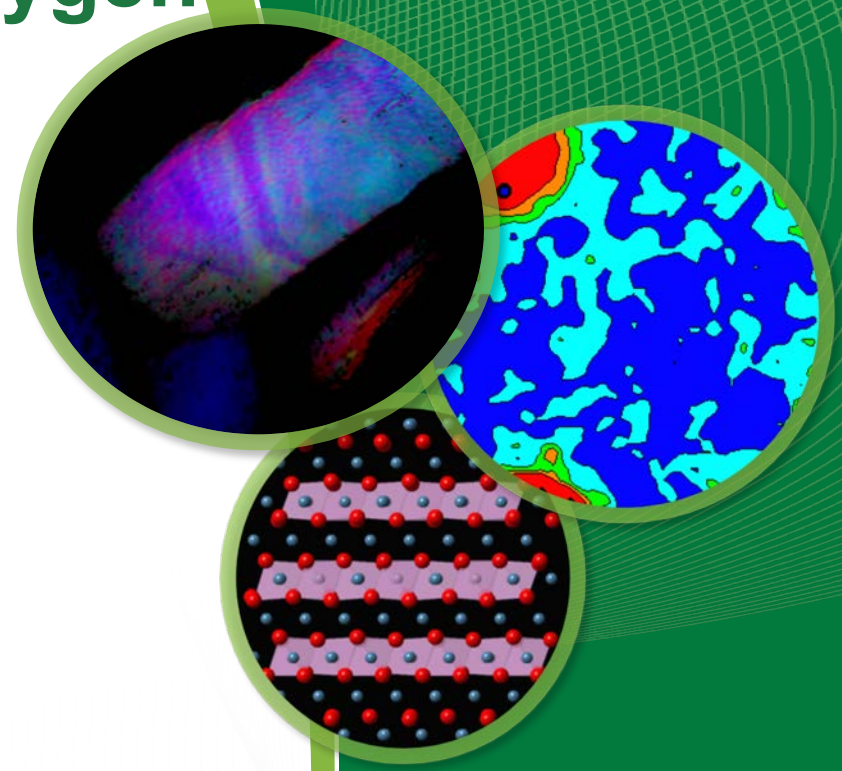
High Capacity Multi-Lithium Oxide Cathodes and Oxygen Stability



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Oak Ridge National Laboratory

2017 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 7, 2017 **Project ID: ES106**

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OAK RIDGE National Laboratory

Overview

Timeline

- Project start date: Oct. 1, 2015
- Project end date: Sept. 30, 2018
- Percent complete: 65%

Barriers

Performance: High energy density for PEV applications with cell level targets ≥ 400 Wh/kg and 600 Wh/L
Life: More than 5000 deep discharges (SoC range) over the entire life
Safety: Thermally stable and abuse tolerant

Budget

- FY16 Funding: $ 400K
- FY17 Funding: $ 400K

Partners

- *Pacific Northwest National Laboratory*
  Electron Microscopy
- *Brookhaven National Laboratory*
  Synchrotron X-ray diffraction and Microscopy
- *SSRL, SLAC, Stanford CA*
  XANES and X-ray imaging
- *CAMP Facility, Argonne National Laboratory*

Any proposed future work is subject to change based on funding levels

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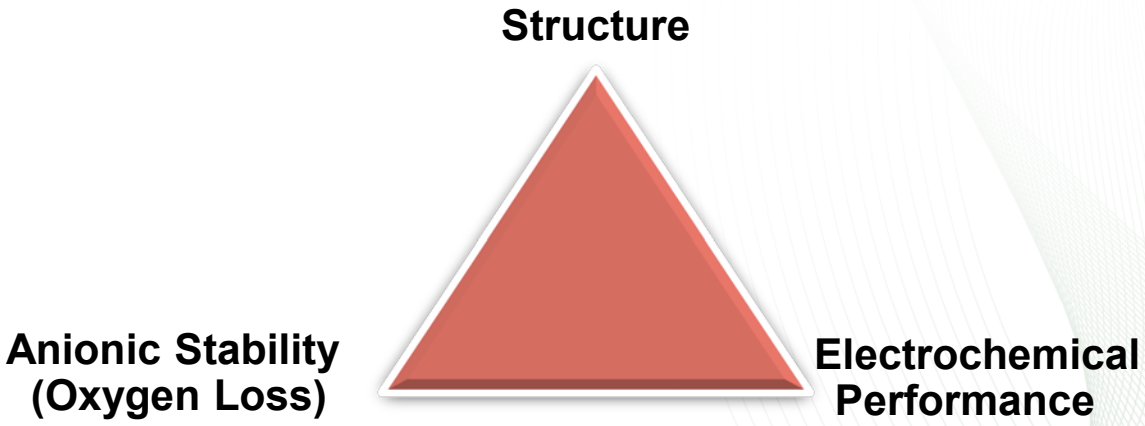
Relevance and Issues

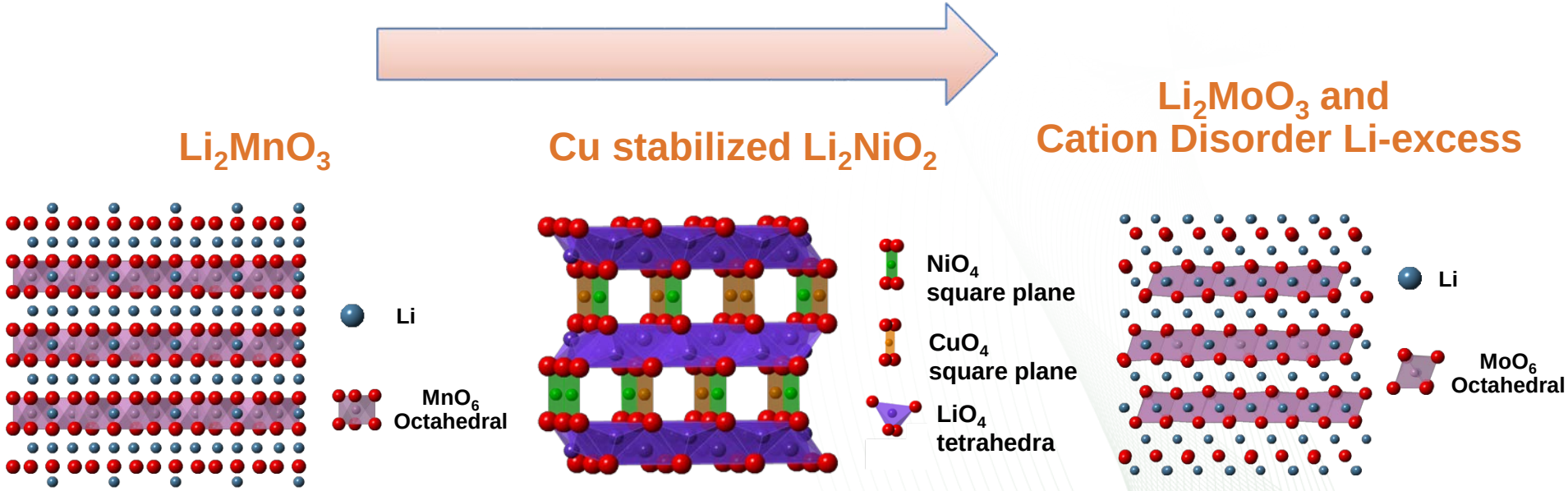
- It's critical to develop practical high-voltage and high-capacity cathode materials for lithium-ion batteries to achieve DOE 2020 cell level targets of 400 Wh/kg & 750 Wh/L or Battery 500 goal of 500 Wh/kg for 1000 cycles.
- Ni-rich NMC and concentration gradient NMC cathodes are currently being developed and commercialized to meet the energy density targets.
- There is substantial evidence from recent experiments that most of the oxide cathodes evolve oxygen either directly or mediated by the carbonate electrolyte when cycled above 4.3 V.
- Oxygen loss from the cathode surface contributes to irreversible capacity loss and structural transformations.



Relevance and Issues

- Oxygen activity and its participation in the redox process is an important barrier for attaining high voltage and capacity in a number of important cathode chemistries.
- Current focus of this work is to understand oxygen loss and structural transformations in high capacity cathodes and develop approaches to address these.

Cathode chemistries studied over the last 2 years



Charge compensation at high voltage during delitihiation involves oxygen participation

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Milestones

Due Date	Description	Status
06/30/2016 (Q3)	Identify the roles of Ni and F towards obtaining reversible redox capacity at higher voltage and stabilizing Ni-rich compositions. Subtask-2.1 XANES, microscopy, and XPS studies.	Complete
09/30/2016 (Q4)	Identify the roles of Ni and F towards obtaining reversible redox capacity at higher voltage and stabilize Ni-rich compositions. Subtask 2.2 Gas evolution and electrochemistry.	Complete
12/31/2016 (Q1)	Synthesize Ni-rich $Li_2Cu_xNi_{1-x}O_2$ cathodes with x = 0.2 and 0.3 and evaluate their high voltage capacity and oxidative stability [> 225 mAh/g, 25 cycles].	Complete/Go-No Go
03/31/2017 (Q2)	Complete in-situ and ex-situ X-ray, neutron, and spectroscopic studies of Ni-rich $Li_2Cu_xNi_{1-x}O_2$ and related high voltage cathode compositions.	Complete
06/30/2017 (Q3)	Synthesize one particular class and composition of cation disordered cathodes: Li_2MoO_3 and Cr - substituted Li_2MoO_2.	In progress
09/30/2017 (Q4)	Complete structural and electrochemical performance analysis of disordered cathodes- Li_2MoO_3 and Cr substituted Li_2MoO_2.	In progress

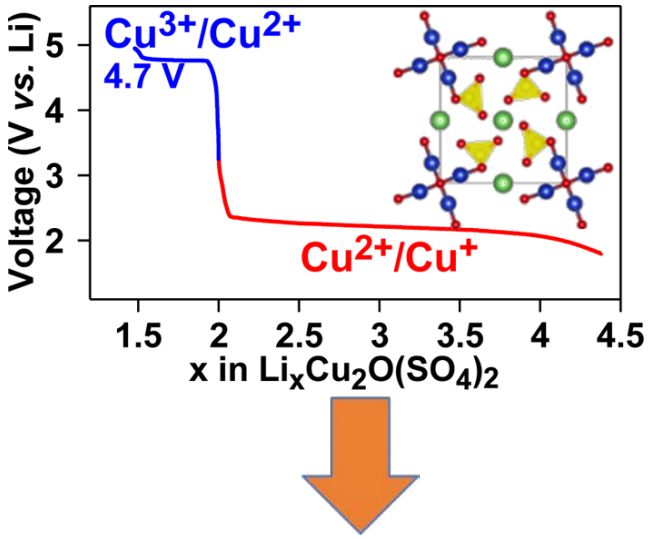
Any proposed future work is subject to change based on funding levels

Approach

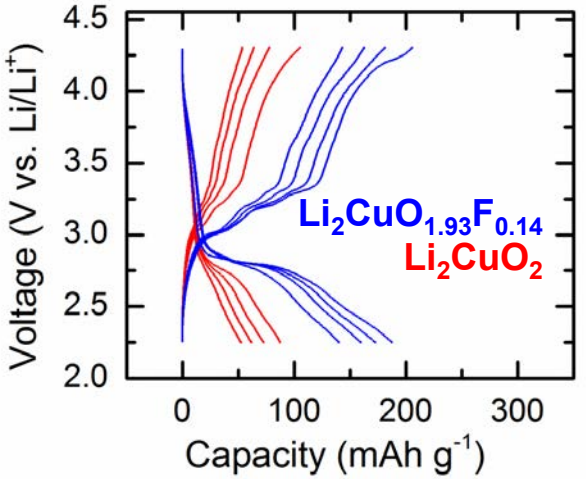
Design and synthesis of high-voltage, high-capacity oxide cathodes guided by *state-of-the-art* characterization and modeling:

- High redox voltage in cathodes is enabled by addressing oxygen stability and/or incorporating polyanionic groups.
- Synthetic approaches include anionic substitution and advanced coatings to stabilize the interface and bulk structure.
- Structural and interfacial changes are correlated with electrochemical performance.
- Diagnostic tools include a suite of microscopic and spectroscopic techniques.

Example :



Fluorination is a simple case of anionic substitution to address oxygen stability.



Unpublished 2017

Can we think of a stabilized oxide framework with redox active $Ni^{3+} \rightarrow Ni^{4+}$ / $Cu^{2+} \rightarrow Cu^{3+}$?

Sun and Tarascon, Chem. Mater. 2015, 27, 3077−3087

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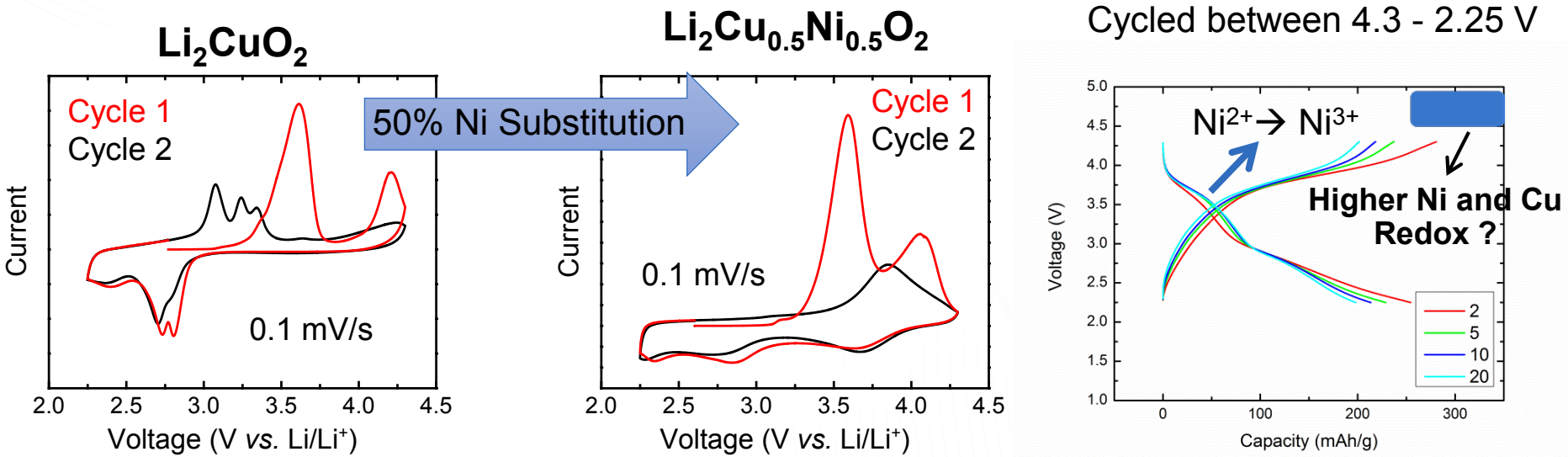
Copper Stabilized Li_2NiO_2 Solid Solutions: Key Points

- Synthesized Ni-rich $Li_2Cu_xNi_{1-x}O_2$ solid solution, x = 0.5 - 0.3 using solid state and sol-gel methods.
- Cu stabilization improves electrochemical stability compared to parent phases Li_2NiO_2 and Li_2CuO_2, but oxygen loss occurs before accessing higher oxidation states ($Cu^{2+/3+}$; $Ni^{3+/4+}$).



Structural transition and gas evolution during 1st charge cycle similar to lithium-excess TM oxides

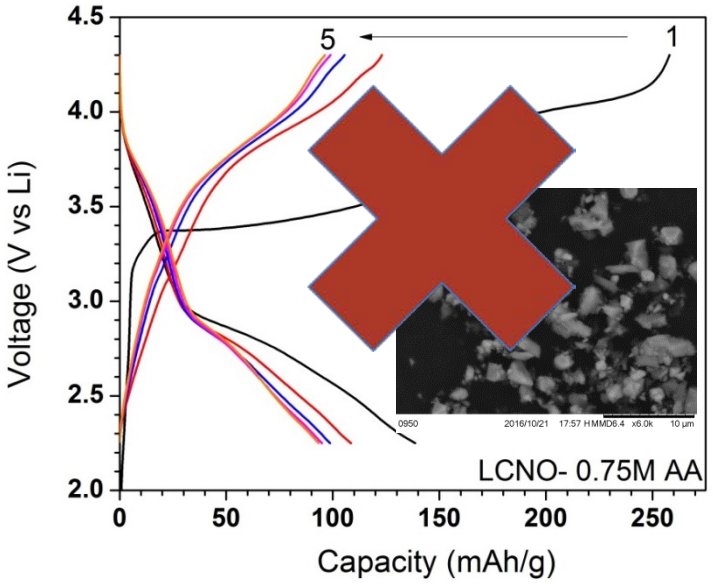
Synthesis and electrochemical results reported in AMR FY 16

High Ni-content $Li_2Cu_xNi_{1-x}O_2$ Compositions Synthesized

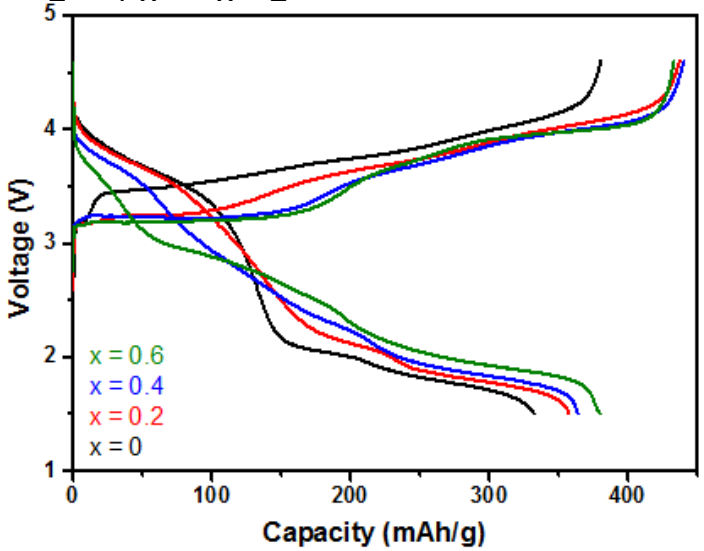
- As an alternate route, $Li_2Cu_xNi_{1-x}O_2$ (LCNO) solid solutions were synthesized via a sol-gel method using adipic acid as a chelating agent to reduce primary particle size with carbon coating.

- LCNO prepared through the sol-gel method showed lower capacity and poor cycle life for one of the compositions, $Li_2Cu_{0.4}Ni_{0.6}O_2$, with Li_2CO_3 as the major impurity phase. This method was not pursued further.

Sol-gel : $Li_2Cu_{0.4}Ni_{0.6}O_2$



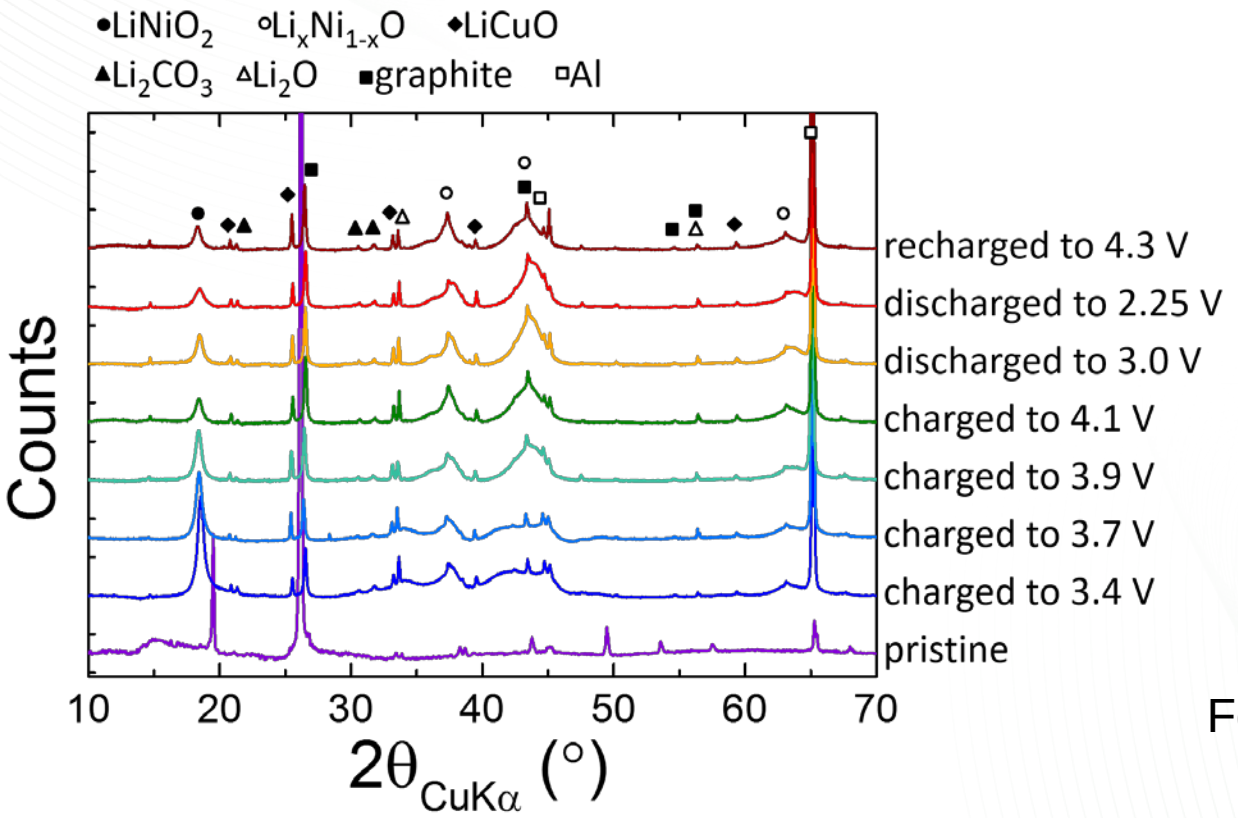
$Li_2Ni_{1-x}Cu_xO_2$ by solid state reaction



Dr. Wei Tong, Lawrence Berkeley National Laboratory

Understanding and addressing the structural transitions and O_2 evolution during 1st charge cycle is key for electrochemical reversibility in high capacity Li- excess and multi-lithium TM oxides.

Ex-situ X-ray Diffraction - $Li_2Cu_{0.5}Ni_{0.5}O_2$



Pristine - $Li_2Cu_{0.5}Ni_{0.5}O_2$
Orthorhombic (*Immm*)

↓ **0.5 Li**

Layered ($R\bar{3}m$) $LiNiO_2$ +
cubic $Li_xNi_{1-x}O$ + LiCuO

↓ **Further delithiation**

↓ **Discharge**

Does not return to *Immm*
Forms nanocrystalline domains

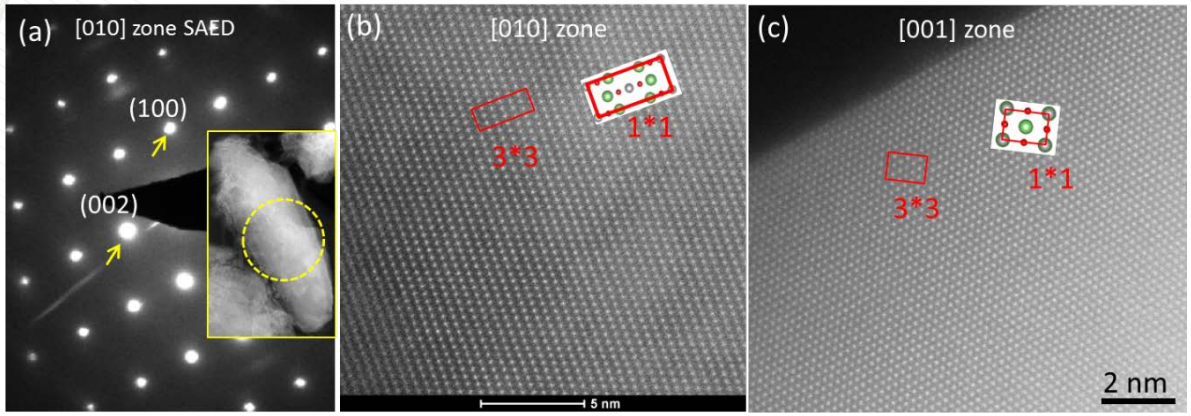
In situ Raman study reported earlier confirms ex-situ XRD observations.

$Li_2Cu_{0.5}Ni_{0.5}O_2$ is a model system studied here, but we notice similar structural changes in a host of multi-lithium TM oxides.

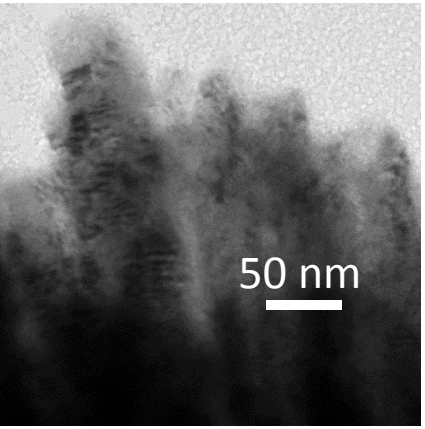
Ruther, R. E. *et al. Chemistry of Materials* **2017,** *29* (7), 2997-3005

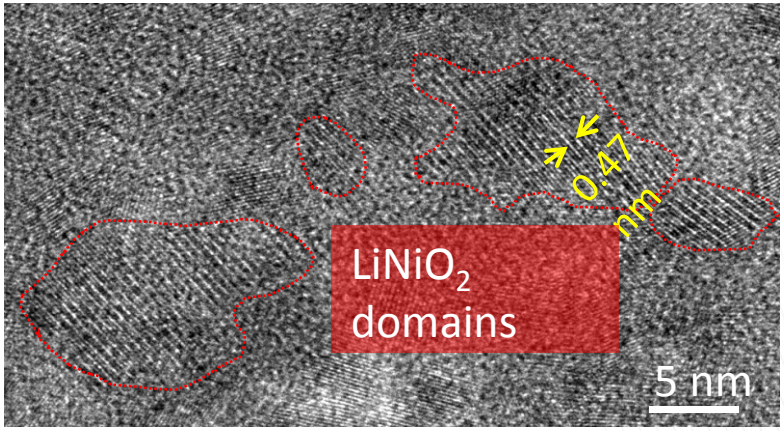
Apart from structural changes we also observed exfoliation and loss of crystallinity with cycling.

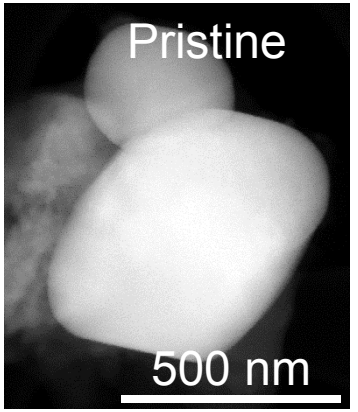
Pristine $Li_2Cu_{0.5}Ni_{0.5}O_2$

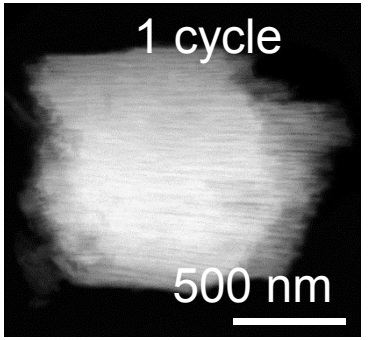


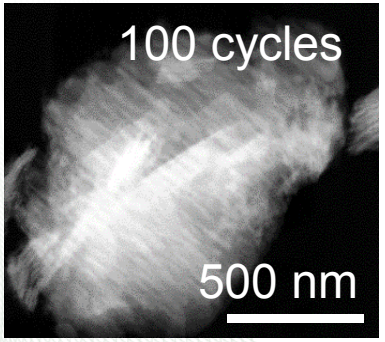
After 1 full cycle





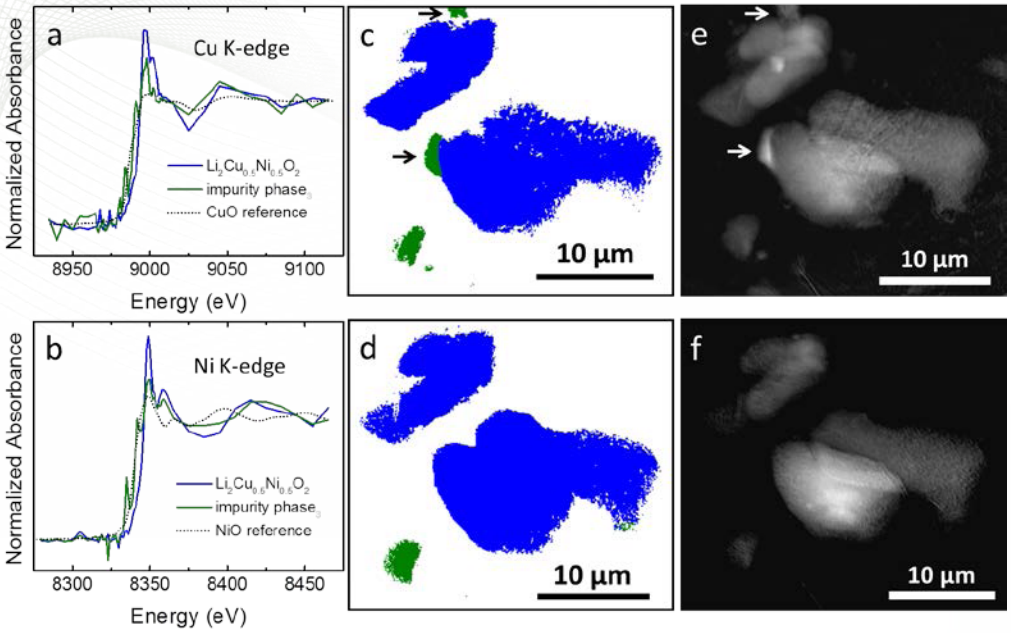




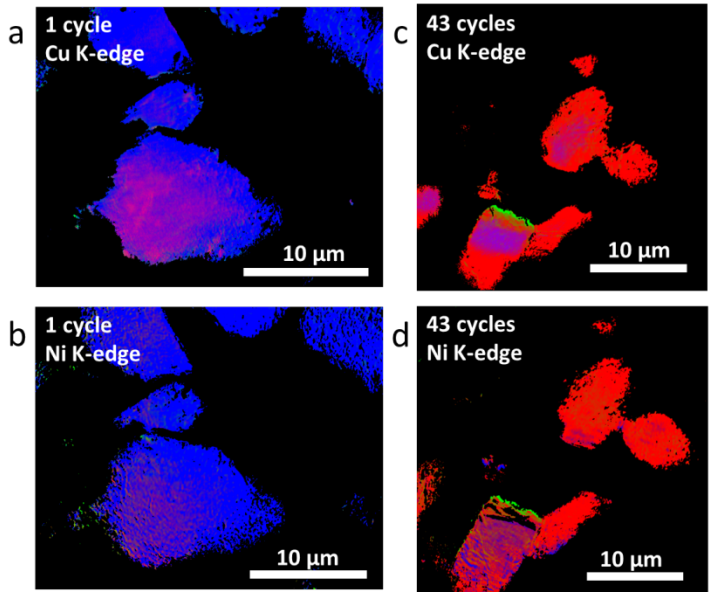


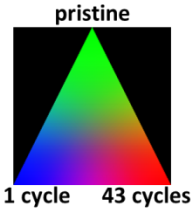
Collaboration with Chongmin Wang and Pengfei Yan, PNNL
Ruther, R. E. *et al. Chemistry of Materials* **2017,** *29* (7), 2997-3005

XANES microscopy is sensitive to amorphous and nanocrystalline phases and impurities that techniques like X-ray diffraction cannot detect.



Pristine $Li_2Cu_{0.5}Ni_{0.5}O_2$ has local Cu and Ni rich impurities mostly Li_xNiO or pure oxides of Ni and Cu



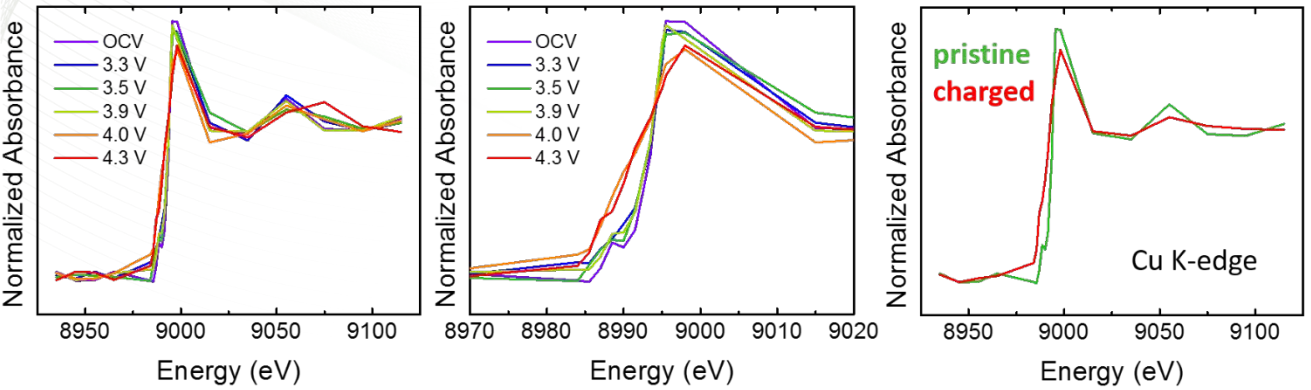


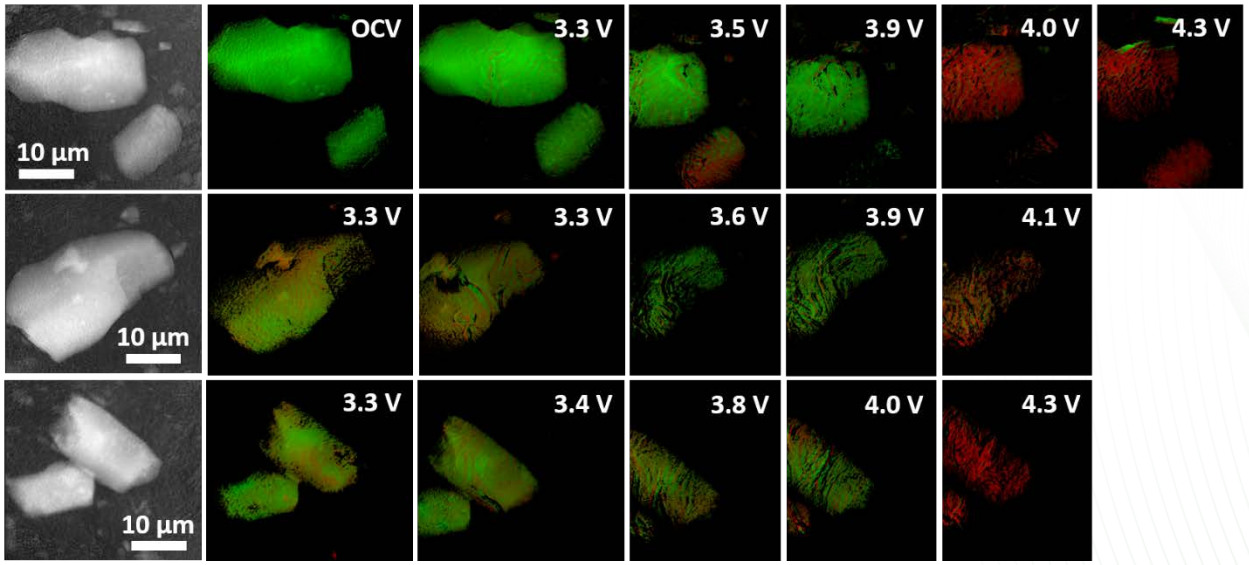
XANES mapping of Ni and Cu K edges Show changes in structure & coordination after 1st full cycle (details in technical backup slides)

Ruther, R. E. *et al. Chemistry of Materials* **2017,** *29* (7), 2997-3005

In situ XANES microscopy reveals phase changes and spatial distributions within $Li_2Cu_{0.5}Ni_{0.5}O_2$ particles.

Copper K-edge



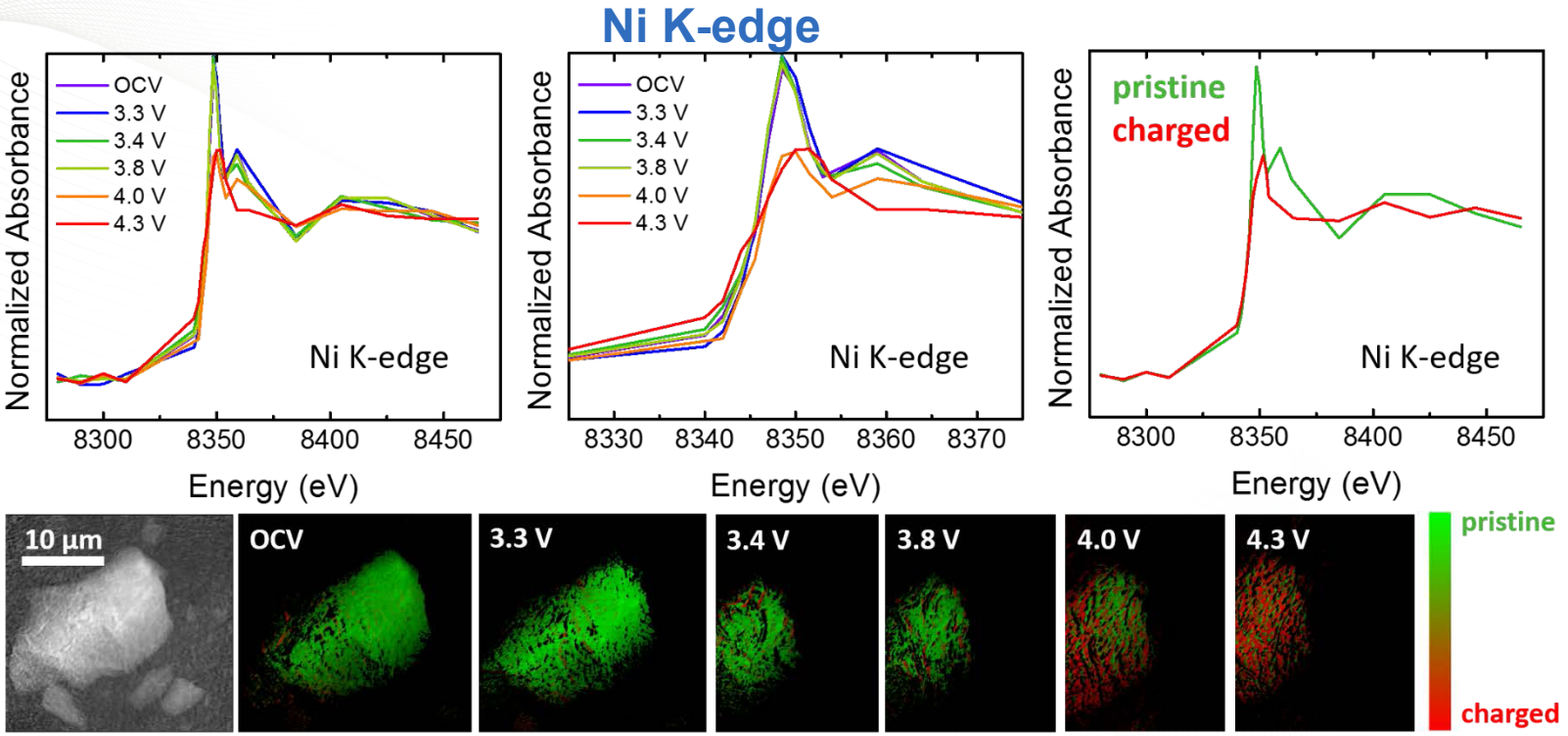


Summary

1. Cu K-edge shifts > 4 V to lower energy.
2. Shift does not correspond to Cu^{2+} to Cu^{3+} oxidation.
3. Shift could mean structural transformation occurs without formal change in oxidation state

Ruther, R. E. *et al. Chemistry of Materials* **2017,** *29* (7), 2997-3005

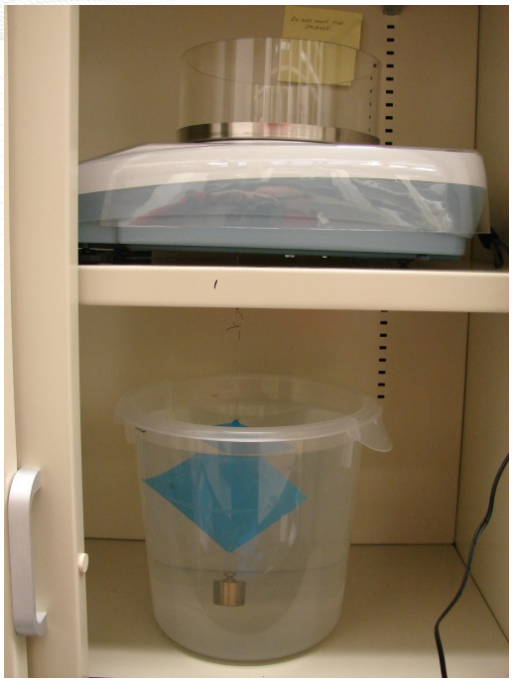
In situ XANES microscopy reveals phase changes and spatial distributions within $Li_2Cu_{0.5}Ni_{0.5}O_2$ particles.



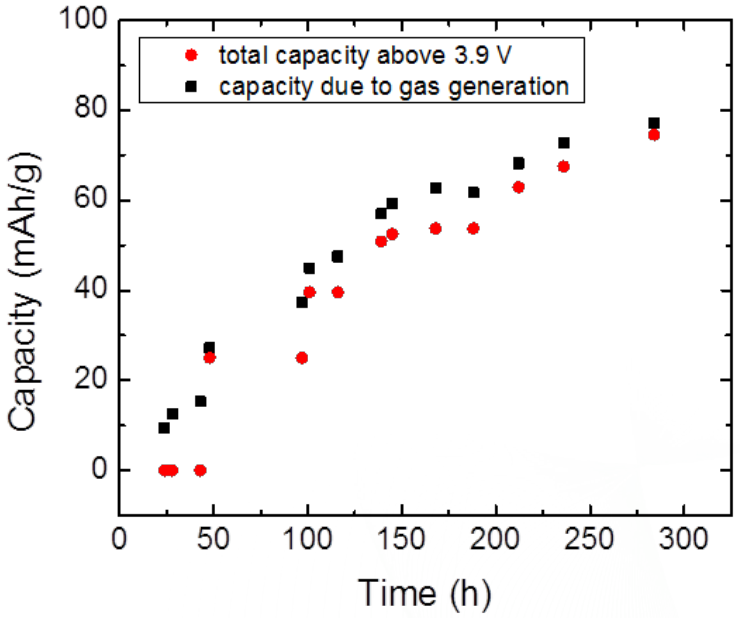
- Ni K-edge shift shows the same trend as Cu; noticeable shift after 4 V to lower energies.
- These shifts occur around the same voltage where we see substantial gas evolution.

Ruther, R. E. *et al. Chemistry of Materials* **2017,** *29* (7), 2997-3005

Capacity of $Li_2Cu_{0.5}Ni_{0.5}O_2$ above 3.9 V is due to gas evolution.



Δm = 1 mg = 1 µL of gas

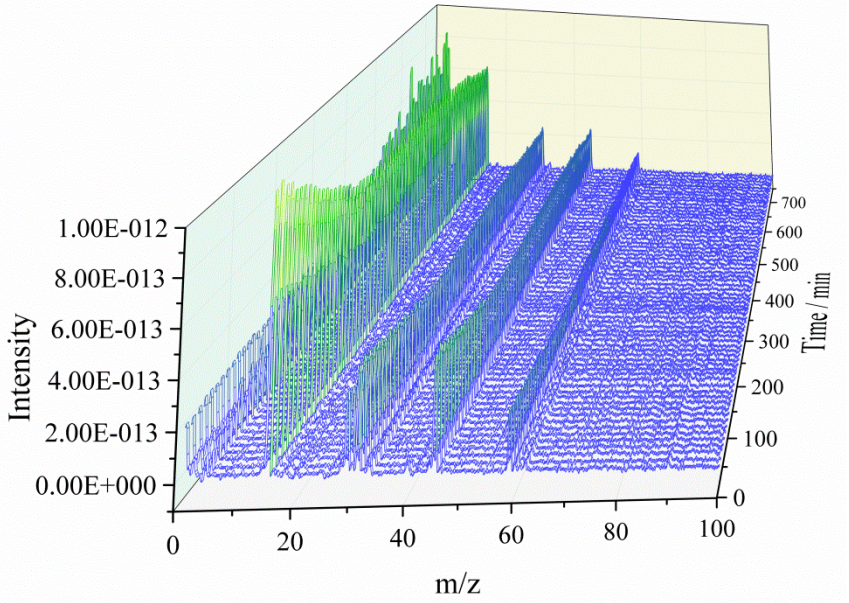


- Gas evolution in pouch cells was quantified using Archimedes' principle.
- $Li_2Cu_{0.5}Ni_{0.5}O_2$ is stable against oxygen release up to extraction of one lithium per formula unit.
- All capacity extracted above 3.9 V can be attributed to gas evolution, assuming 4 e^- per mole of gas.
- O_2 and CO_2 were main gasses detected by mass spectrometry (G. Veith).

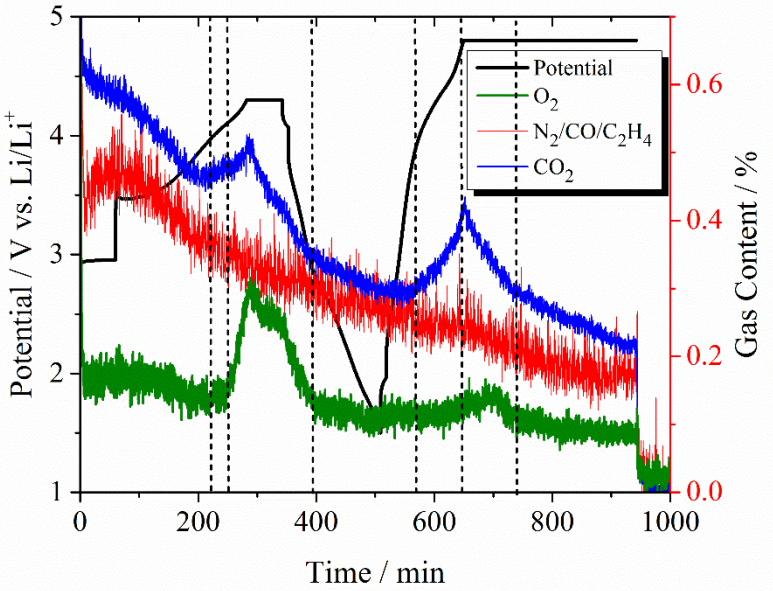
Ruther, R. E. *et al.*, *Chemistry of Materials* **2015,** *27* (19), 6746-6754

Gas Evolution of $Li_2Cu_{0.5}Ni_{0.5}O_2$ Cathodes

In-situ mass spectrometry was used to determine the types/amounts of gases evolved from $Li_2Cu_{0.5}Ni_{0.5}O_2$ cathodes during cycling.



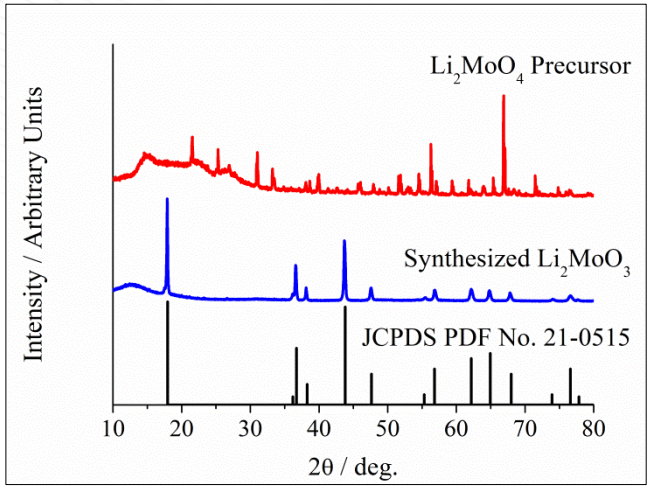
Data Processing



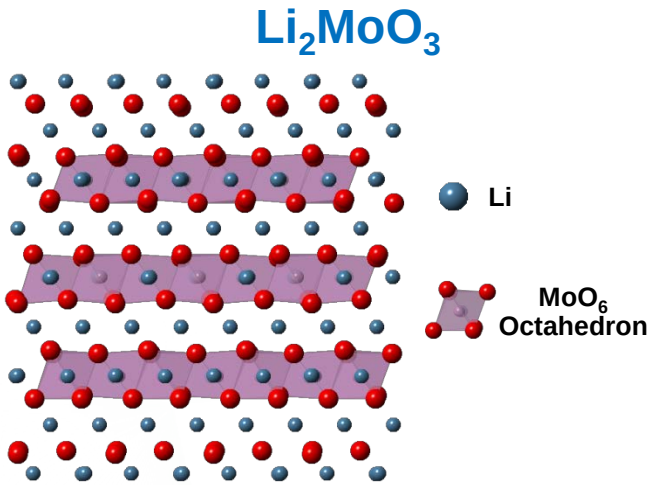
- O_2 and CO_2 were main gases detected.
- In-situ gas evolution studies allow us to monitor electrolyte decomposition products and oxygen evolution from the cathode lattice in an operating battery.
- Similar results obtained from *in situ* DEMS work on $Li_2Cu_{0.2}Ni_{0.8}O_2$ from LBNL. (Wei Tong and Bryan McCloskey)

Li_2MoO_3 Synthesis and Electrochemical Characterization

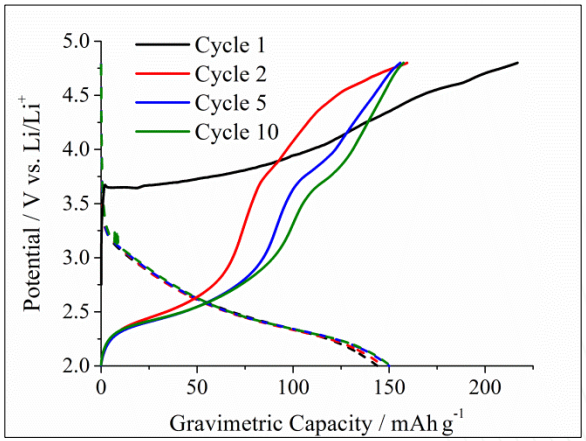
Li_2MoO_3 has improved lattice oxygen stability[1] compared to Li_2MnO_3. Thus, a synthesis procedure was developed to produce Li_2MoO_3 for Li-excess composite high-voltage cathodes.

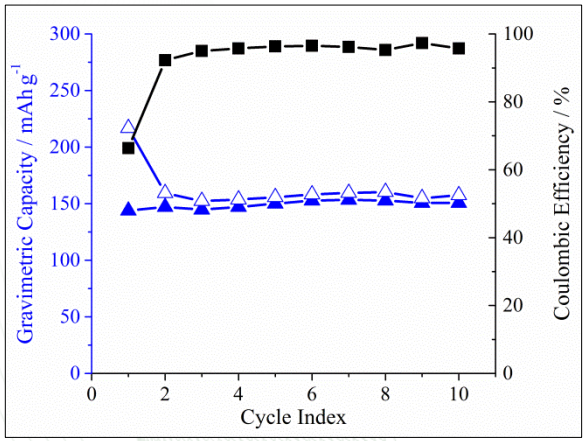


Synthesized Li_2MoO_3 has desired crystal structure ($R\bar{3}m$ spacegroup)



Half-Cell Characterization (2.0 – 4.8 V at 10 mA/g)



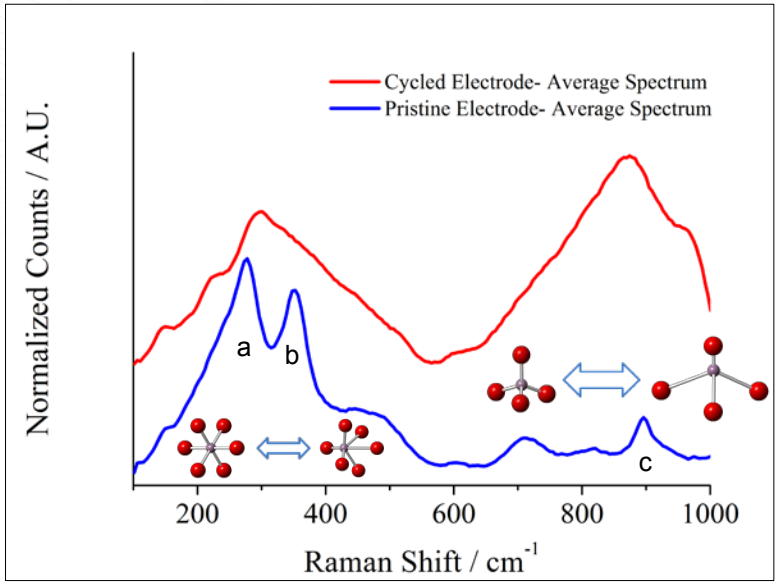


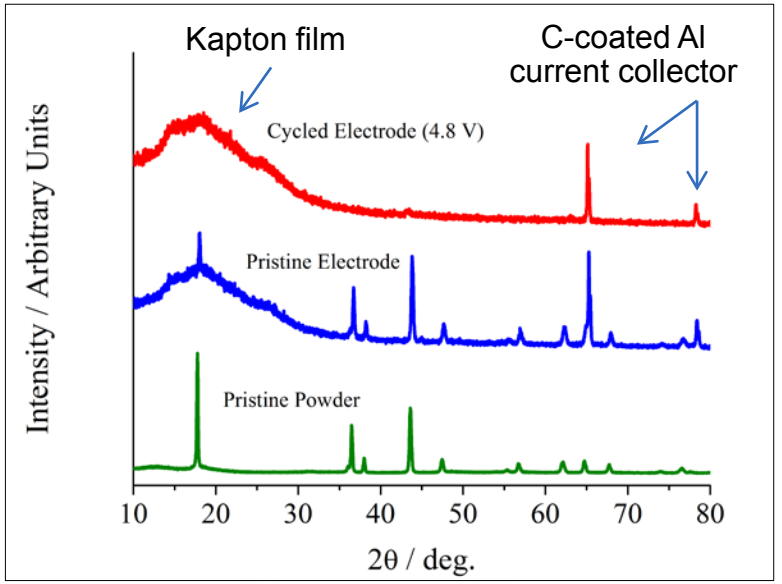
[1] J. Ma et al. *Chem. Mater.* **2014**, 26, 3256-3262.

Ethan Self et al. Unpublished 2017

Ex-Situ Raman and XRD of Li_2MoO_3 Cathodes

Li_2MoO_3 cathode was cycled between 2.0 – 4.8 V at 10 mA/g for 10 cycles. The cell was disassembled after recharging to 4.8 V. The Li_2MoO_3 electrode was rinsed with DMC before post-mortem analysis.





Raman Peak in Pristine Li_2MoO_3	Raman Shift (cm^{-1})	Assignment[1]
a	277	Li_2MoO_3 (Mo-O-Mo bridging species in Mo_3O_{13} clusters)
b	351	Li_2MoO_3 (Mo=O in MoO_6 octahedral)
c	896	Li_2MoO_4 (MoO_4 tetrahedral in Li_2MoO_4). Li_2MoO_4 is a minor impurity which was not detected by XRD.

[1] J. Ma et al. *J. Power Sources* **2014**, 258, 314-320.

- Post-mortem analysis suggests that Li_2MoO_3 becomes amorphous during cycling.
- Future experiments using *in-situ* XRD, *in-situ* Raman, and *in-situ* mass spectrometry will elucidate the details of this transformation.

Response to Reviewers Comments

This project was not reviewed in 2016.

All Comments from 2015 were addressed in 2016 presentation.

Collaborations and Coordination with other Institutions

Pacific Northwest NATIONAL LABORATORY

Electron Microscopy
Drs. Chongmin Wang & Pengfei Yan

BROOKHAVEN NATIONAL LABORATORY

In-operando X-ray Synchrotron Studies and Microscopy
Dr. Feng Wang

SLAC NATIONAL ACCELERATOR LABORATORY

Synchrotron X-ray microscopy and 3D microstructure
Dr. Johanna Nelson Weker

BERKELEY LAB
Lawrence Berkeley National Laboratory

Modeling and oxygen activity of Li-excess compositions

OAK RIDGE National Laboratory

Remaining Barriers and Challenges

- Determine if anionic substitution like fluorination can suppress oxygen evolution and enable high voltage operation.
- Investigate oxygen stability in Li-excess cation disordered cathodes.
- Determine the stability of cathode powders or electrodes in air, especially with respect to Li_2CO_3 formation on surface.
- Optimize the synthesis and electrochemical performance of cation disordered Li-excess compositions: Li_2MoO_3 and Li-excess Cr-substituted $LiMoO_2$.
- Develop approaches to mitigate lattice oxygen loss and improve structural stability of the cathode surface.

Any proposed future work is subject to change based on funding levels

Proposed Future Research

Synthesis and Optimization of High Capacity 2-Lithium Oxide Cathodes: $Li_2M^{I}M^{II}O_3$ and $Li_2M^{I}M^{II}O_3$

M^{I} – M^{II} : Ni, Cu, Mo, Mn, Cr

These are crystalline, ordered, stoichiometric compositions to begin with

Lithium-excess disordered compounds

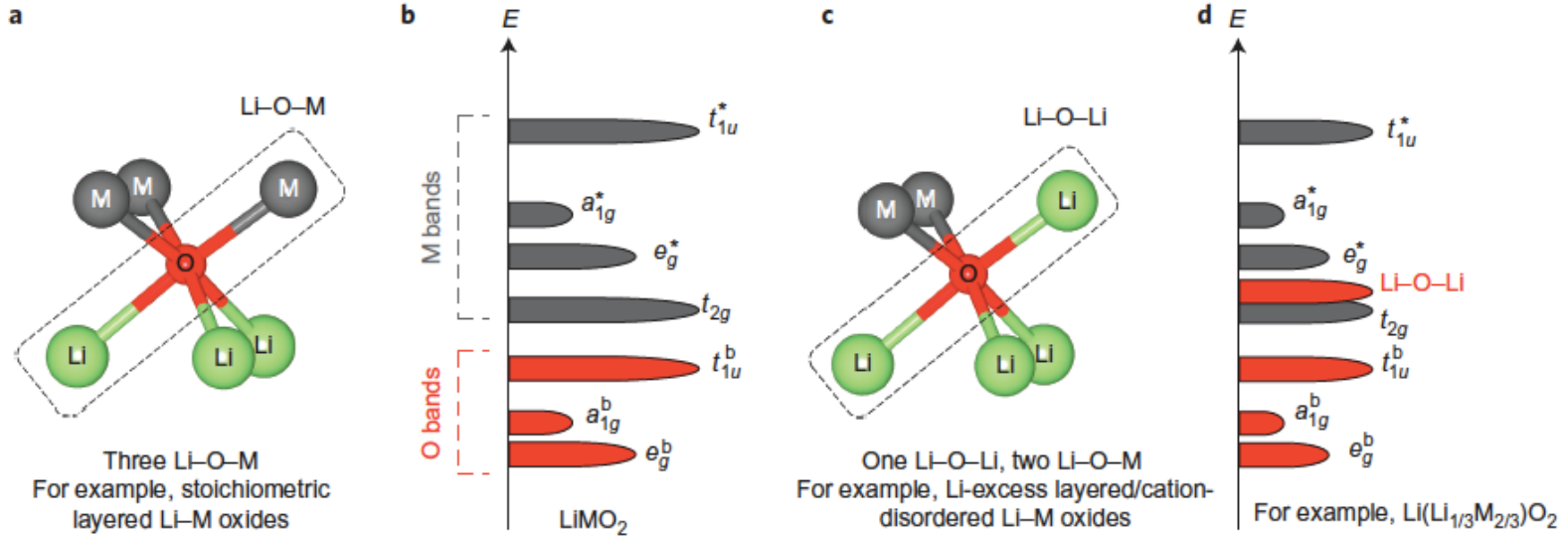
$Li_{1+x}(Mn,Co,Ni)O_2$; $Li_{1+x}MoCrO_2$; $Li_{1.25}Nb_{0.5}Mn_{0.5}O_2$

$Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$

Goals

- Increase oxidative stability and attain extra capacity.
- Understand the role of disorder in increasing the lithium diffusion pathways.
- Quantify oxygen participation in the redox process.

Origin of extra capacity in disordered cathodes



Any proposed future work is subject to change based on funding levels

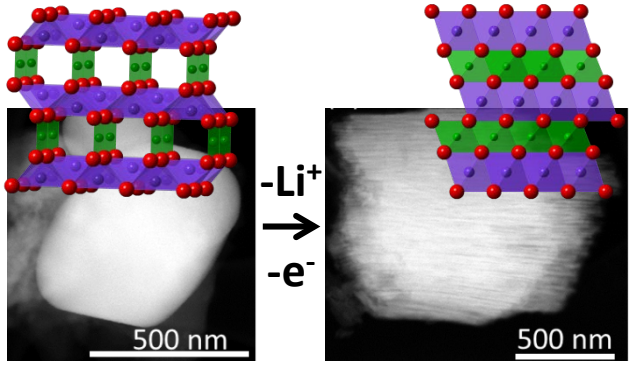
Seo, Ceder et al. Nature Chemistry, 8, 692 (2016)

Summary

Technical Approach:

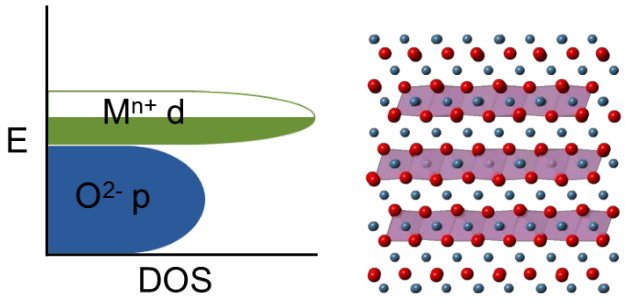
Synthesis and in-depth analysis of lithium-excess and multi-lithium chemistries for high voltage, high capacity cathodes

- Model driven synthetic approaches : solution-based, sol-gel and solid state methods.
- Diagnostic tools include a suite of microscopic, spectroscopic, and analytical techniques.
- Emphasis is placed on understanding and preventing oxygen loss at high voltage



Accomplishments:

- Identified chemical and structural changes that occur in $Li_2Cu_{0.5}Ni_{0.5}O_2$ under in situ conditions and mapped out phase transformations using TXM-XANES.
- Unraveled mechanisms of electrochemical activity and degradation of $Li_2Cu_xNi_{1-x}O_2$ cathodes using a combination of X-ray and neutron diffraction, *in situ* Raman spectroscopy, electrochemistry, gas evolution experiments, and TEM.
- Synthesized Li_2MoO_3 as an analogue to Li_2MnO_3 with greater stability of lattice oxygen and completed initial characterization with electrochemistry, XRD, and Raman.

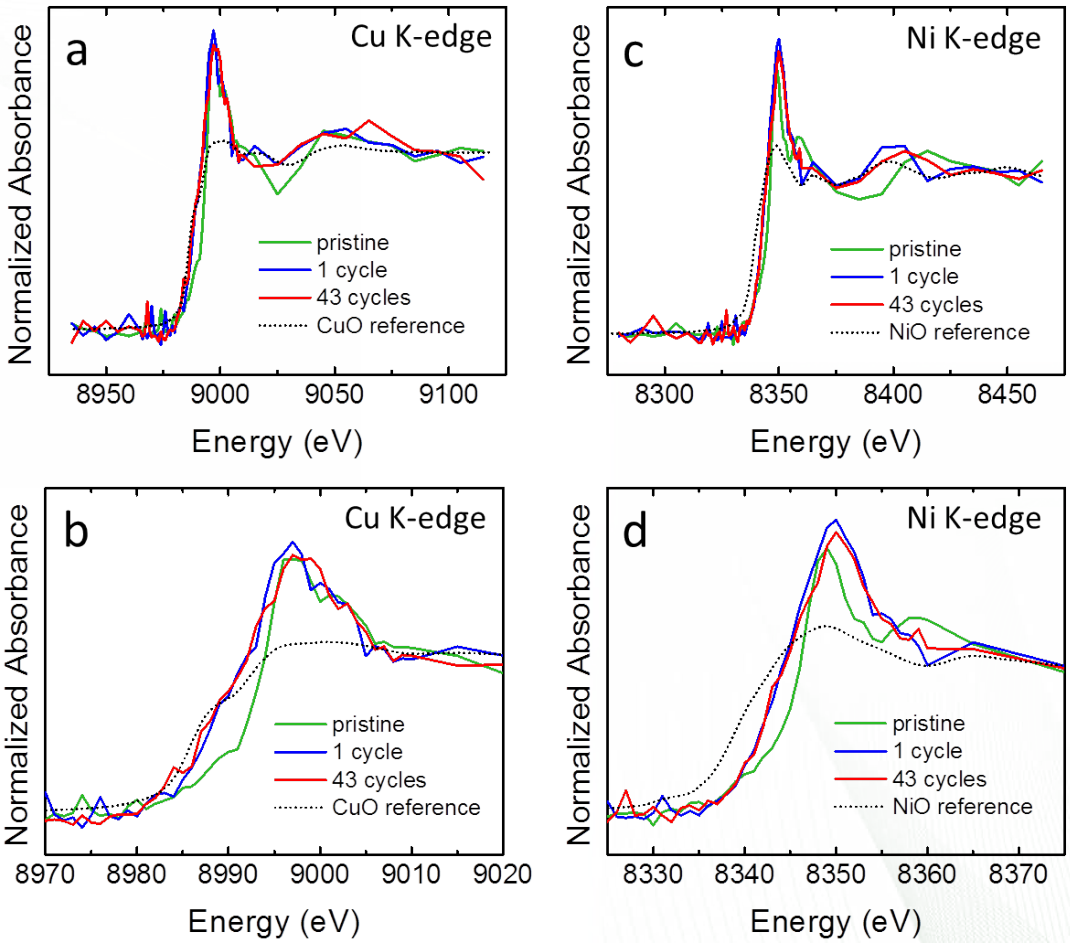


Ongoing work:

- Optimize the synthesis and processing of cation disordered Li-excess compositions, Li_2MoO_3 and Cr-doped Li_2MoO_3.
- Understand structural transformations in Li_2MoO_3 *in situ* using XRD, Raman, and gas monitoring.
- Investigate oxygen stability in disordered cathodes and continue to develop approaches to prevent oxygen loss.

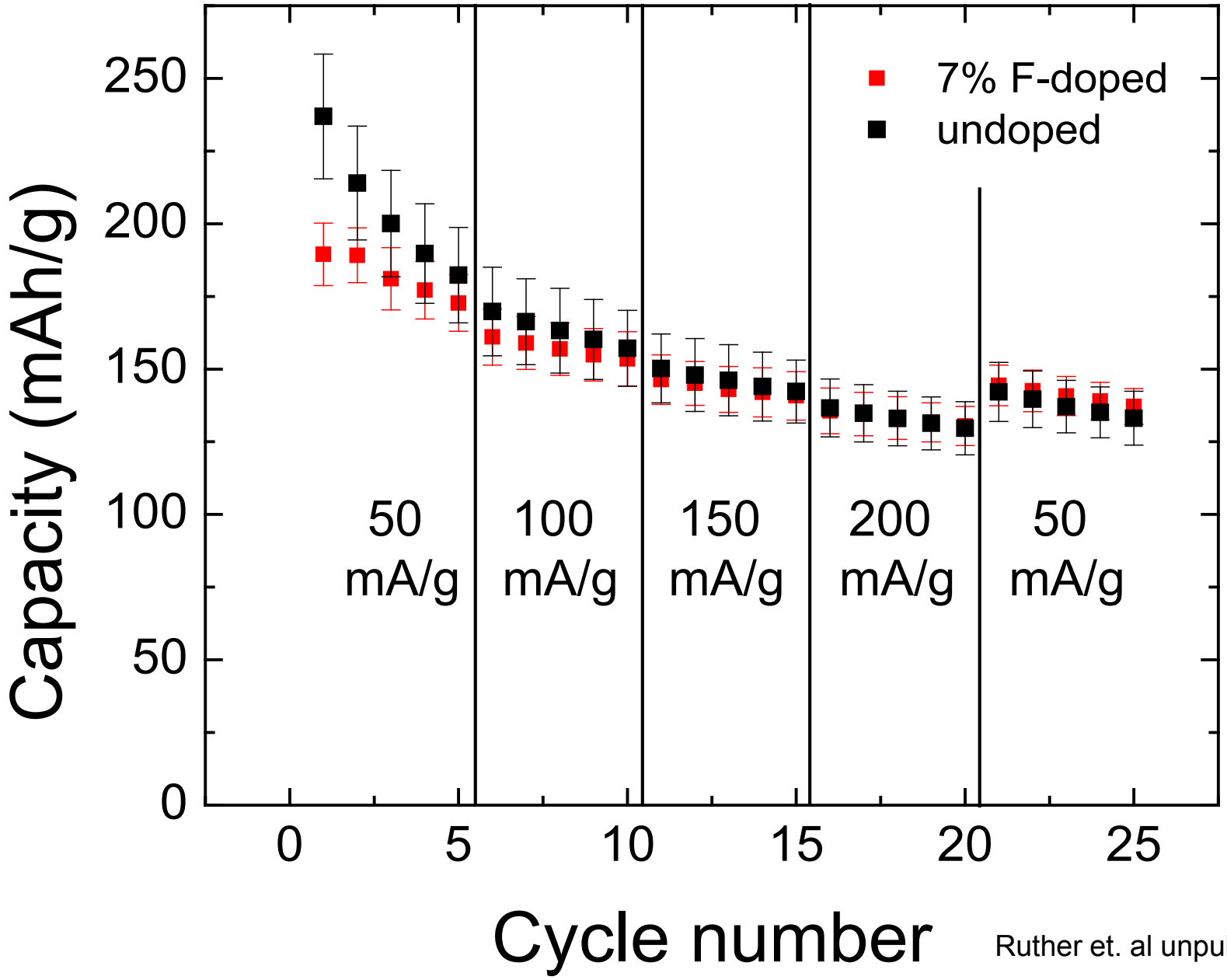
Technical Back-up

Ex-situ XANES Spectra : $Li_2Cu_{0.5}Ni_{0.5}O_2$



These spectra are used to generate the Ni and Cu K edge XANES 2D maps as shown in slide # 11

Li_2CuO_2 and F- substituted Li_2CuO_2 have similar rate and capacity retention



Ruther et. al unpublished 2016